

NO and N₂O decomposition and their reduction by hydrocarbons over Fe–Zn manganite spinels

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Abstract

In this work the catalytic behaviour of zinc manganite-based catalysts doped with iron in small amounts is reported for the reduction of NO by propane and propene. All catalysts are monophasic and are characterized by a spinel structure. On the most representative catalysts the NO and N₂O decomposition and the reduction of N₂O by propane and propene were also investigated. The NO reduction by hydrocarbons is enhanced by the presence of iron and the catalytic activity increases on increasing the iron loading. On the other hand, the catalytic activity of N₂O reduction appears to be less sensitive to either the presence of iron and the type of hydrocarbon. Moreover, it is almost comparable to that of N₂O decomposition which, in turn, occurs much easier than the NO decomposition. In all reactions the selectivity to N₂ and CO₂ is almost 1 at the maximum temperature explored of 873 K. Along the NO and N₂O reduction by hydrocarbons iron preserves in some extent the catalyst from reduction which tends to occur in propene at higher temperatures disaggregating the spinel phase into a mixture of ZnO and MnO oxides.
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1. Introduction

The removal of gaseous pollutants from atmosphere is a world-wide problem of immense concern and many efforts are devoted to find out for it adequate solutions. In particular nitrogen oxides, usually called NO_x, represent a very serious source of pollution. Indeed NO is significantly present in the exhaust gases produced by both stationary and mobile sources and is considered one of the most dangerous pollutants being responsible for acid rain and ozone formation. Also N₂O has a detrimental impact on the environment mainly for having a very large greenhouse effect. Therefore its emission is requested to be drastically lowered in the next future. Many catalytic systems have been investigated to convert NO and N₂O into N₂ and, with this respect, manganese-based catalysts have recently gained a renewed attention [1–13].

Some years ago we started a research project concerning the preparation and characterization of transition metal

ion-containing zinc manganites because they seemed to be catalysts of interest in reactions for the abatement of NO and N₂O. In particular, we tested the NO and N₂O decomposition and their reduction by propane and propene. Even though the selective catalytic reduction by hydrocarbons (HC-SCR) is the most investigated reaction to remove NO_x from oxygen-rich exhaust, its chemistry is very complex and, consequently, the investigation of more simple reactions like the NO and N₂O reduction by hydrocarbons can be very useful for understanding the elementary steps and, therefore, the mechanism involved in the more complex SCR reaction. To this purpose also the NO and N₂O decomposition, interesting by themselves for their direct practical applications, can provide valuable information. Zinc manganite doped with transition metal ions has been chosen as catalyst of interest because it has a spinel-like structure which offers the possibility of replacing cations in both the tetrahedral and octahedral sites available in the spinel crystal lattice. This feature makes these solids very suitable for fundamental studies devoted to find a correlation between structural and catalytic properties of the catalyst. Along the project, three different sets of samples were prepared by doping zinc manganite with copper, cobalt and iron. Each metal was

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loaded in the spinel at different amounts in order to investigate the effect of the metal content on the catalytic activity. Results concerning the preparation, characterization and catalytic behaviour of copper–zinc and cobalt–zinc manganites have been already published [14–17]. Finally, we started an investigation over iron–zinc manganites and some findings dealing with their preparation and characterization have been reported elsewhere [18–19].

In this paper, representing the concluding piece of work of our project on the zinc manganite system doped with transition metal ions, the complete study of the catalytic investigation of the NO and N₂O reduction by propane and propene is reported. Moreover, also the NO and N₂O decomposition was investigated for some representative samples. Aim of this work is to present extensively all the results obtained on the catalytic behaviour of the Fe–zinc manganite system. In particular, it is shown the dependence of the catalytic activity on the iron loading and in one important case the different effect of iron, if compared to copper and cobalt, on the N₂ selectivity. Finally, the reaction mechanism and the role of either Mn³⁺ ions as well as the role of surface released oxygen species are discussed in more detail with respect to the previous related papers.

2. Experimental

2.1. Catalyst preparation and characterization

Rhodochrosite-like (MnCO₃) monophasic carbonate precursors were obtained by coprecipitation at constant pH 8 starting from an aqueous solution of metal nitrates. In order to have the spinel stoichiometry, the Mn/(Fe + Zn) ratio was fixed at 2 while the iron loading was varied by changing the Fe/(Fe + Zn) molar ratio to obtain the 0.01, 0.05 and 0.10 values. The final catalysts were obtained by thermal decomposition of the precursors in air at 973 K for 24 h and will be hereafter labelled as ZnMn–Fe(*x*) where *x* = Fe/(Fe + Zn) = 0, 0.01, 0.05, 0.10 with reference to the iron content. In all cases the final catalysts were monophasic and formed by a tetragonal ZnMn₂O₄ spinel-like phase. Both the precursors and the catalysts were characterized by many techniques and details have been reported elsewhere [18,19].

2.2. Catalytic tests

The catalytic tests were carried out in the steady-state flow mode. The apparatus consists in a pyrex-glass vacuum line to which an in-flow system made by valves and capillary tubing in stainless steel was connected to perform the reaction studies under flowing conditions. The reactant gases (NO, 2% in He; N₂O, 4% in He; C₃H₈, 1% in He; C₃H₆, 1% in He) were high purity grade (99.999%) and were used as received. Ultrapure grade helium was used as diluent. The flow of each gas was fixed and held constant with a four-channel electronic mass-flow controller (Brooks Instruments, Model 5850S). The effluent gas was sampled through an Alltech CTR-1 column

and analyzed by an on-line gas chromatograph (DANI Instruments, Model 3800) provided with a hot wire detector (DANI Instruments, Model HWD 686). The HWD output was digitally acquired *via* a personal computer by using a program (Chrom-Card, Fisons) by which the qualitative and quantitative analysis was also made. A temperature controller (Leeds and Northrup Instruments, Model Electromax V Plus) was used both for increasing the furnace temperature by linear heating rates (10 K/min) and for keeping it constant at any selected value. The catalysts were loaded in a 1 cm diameter quartz-glass reactor (50–250 mg) and undergo a standard pre-treatment that was made *in situ* in the vacuum line of the apparatus. The pre-treatment consisted in the following four steps: (a) heating in flowing 10% O₂ in He at 923 K overnight, (b) cooling in O₂ at 573 K, (c) a He flushing for about 15 min at 573 K and, finally, (d) cooling at room temperature before the reaction was initiated. In all experiments the NO, N₂O and hydrocarbon concentrations were kept constant at 0.46% molar in He. The typical reactant blend, 0.46% NO (or 0.46% N₂O) + 0.46% C₃H₈, or 0.46% C₃H₆ + He balance, was passed through the catalyst while the temperature was linearly increased, or decreased, in the range of temperature 523–873 K with a 0.5 h isothermal steps at any selected temperature during which the analysis of the effluent gas was made. In the case of the decomposition reaction the concentration of both NO and N₂O in the reactant stream was fixed at 0.46% (0.46% NO or 0.46% N₂O + He balance) as for the reduction experiments. In any experiment the total flow rate was kept constant at 100 mL (NTP)/min and pure He was used to maintain the total pressure at 1 atm. Under this conditions GHSV ranged from 12,000 to 60,000 h^{−1}, this latter value being fixed in order to obtain conversions low enough (<30%) for calculating reliable apparent reaction rates. Nitrogen and carbon balances were always better than 95%. Blank experiments carried out by flowing the reactant streams over an empty reactor showed that no NO, or N₂O, conversion occurred up to 873 K. For the hydrocarbon conversion, the fractional selectivity to CO₂ is expressed as CO₂ molecules/(CO₂ molecules + CO molecules), while in the case of NO conversion the fractional selectivity to N₂ is expressed as N₂ molecules/(N₂ molecules + N₂O molecules).

3. Results

The main results of the precursor and catalyst characterization, reported in detail elsewhere [19], are summarized in Table 1. XRD reference patterns for MnCO₃, ZnMn₂O₄, ZnO and MnO oxides were taken from literature.¹ Regardless the presence of iron, the precursors were all monophasic and made by a solid solution of zinc, or zinc plus iron, in the MnCO₃ rhodochrosite-like phase. Upon thermal decomposition of the carbonate precursors in air at 973 K, monophasic catalysts were

¹ X-ray powder data file: (a) ASTM 7-268 for MnCO₃ (rhodochrosite); (b) ASTM 24-1133 for ZnMn₂O₄ (hetaerolite); (c) ASTM 36-1451 for ZnO (zincite); (d) ASTM 7-230 for MnO (manganosite).

Table 1
Precursors and calcined catalysts (973 K) main features

Sample	Phases (XRD)		Fe content		Surface area (m ² /g)
	Precursors	Catalysts	wt%	χ_{Fe}^a	
ZnMn–Fe(0)	MnCO ₃ ^b	ZnMn ₂ O ₄ ^c	–	–	6.2
ZnMn–Fe(0.01)	R ^d	S ^e	0.614	0.0101	7.3
ZnMn–Fe(0.05)	R ^d	S ^e	3.127	0.0497	7.9
ZnMn–Fe(0.10)	R ^d	S ^e	6.087	0.1036	6.1

^a $\chi_{\text{Fe}} = \text{Fe}/(\text{Fe} + \text{Zn})$, experimental iron molar ratio.

^b Rhodochrosite reference compound (see footnote 1).

^c Hetaerolite reference compound (see footnote 1).

^d Rhodochrosite-like phase.

^e Tetragonal spinel-like phase.

obtained. They all matched the hetaerolite ZnMn₂O₄ reference compound and were characterized by a distorted tetragonal spinel-like structure in which both tetrahedral (A) and octahedral (B) sites are available for guests cations [19]. In this structure the Zn²⁺ ions are located in the tetrahedral sites and iron entered as Fe³⁺ ions in solid solution occupying the octahedral sites of the spinel lattice [18,19]. It is worth to recall that upon calcination at 973 K a partial self-reduction of the catalysts occurred, as suggested by some results obtained by magnetic measurements [19]. At this relatively high temperature, about 7% of the initial Mn³⁺ ion turned into Mn²⁺ ions with a consequent formation of oxygen vacancies necessary to preserve the charge neutrality of the crystal lattice [19]. It is known that a self-reduction mechanism by increasing the temperature works in the phase conversion of Mn₂O₃, Fe₂O₃ and Co₂O₃ into, respectively, Mn₃O₄, Fe₃O₄ and Co₃O₄ having the spinel structure [19]. We were aware of these phenomena and therefore, in order to prevent uncontrolled changing of the catalyst stoichiometry during catalysis, we have chosen the set of catalysts calcined at 973 K, and not those calcined at 723 K [19]. In this way the maximum temperature of the catalytic runs (873 K) is well below that of the catalyst calcination (973 K).

During prolonged catalytic runs made for the NO and N₂O reduction, a stable catalytic behaviour is observed for all catalysts. A representative example is provided by Fig. 1A and B in which plots of the NO conversion and N₂ selectivity versus time-on-stream are shown for the most rich in iron catalyst, i.e. ZnMn–Fe(0.10), when propane (A) or propene (B) are used as reducing agents. For the NO reduction, the selectivity to N₂ and CO₂ is equal to 1 for all catalysts at the temperature of maximum conversion. In Fig. 2 the Arrhenius plots showing the areal rate of NO reduction by propane (A) and propene (B) are reported for all the iron-containing catalysts and for the undoped ZnMn–Fe(0), used as reference sample. For the sake of comparison, in this figure the points quoting the rate of conversion of NO for the NO decomposition over the ZnMn–Fe(0) and ZnMn–Fe(0.10), taken as representative catalysts, are also shown. The Arrhenius plots make evident some features of the NO decomposition. First, this reaction occurs less efficiently than the NO reduction by hydrocarbons, as clearly indicated by the relative heights of the activity levels for the two reactions. Moreover, a measurable activity for the NO decomposition was detected only at the highest reaction

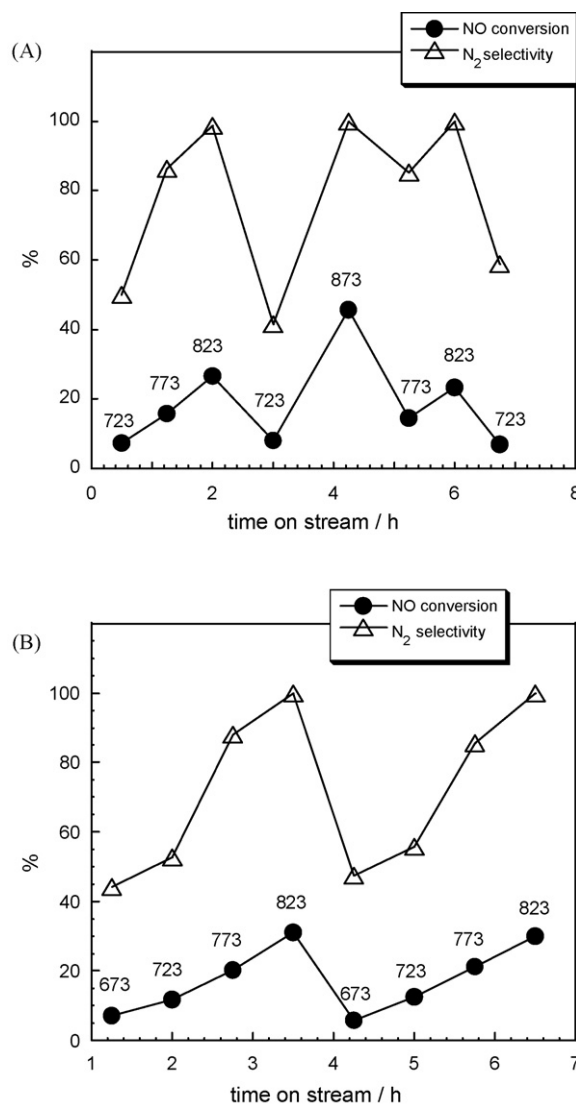


Fig. 1. Activity and selectivity to N₂ vs. time on stream for the NO reduction by propane (A) and propene (B). The numbers inside the plots indicate the reaction temperature (K). Sample: ZnMn–Fe(0.10); ca. 0.05 g. Reactant stream: [NO] = [C₃H₈] = [C₃H₆] = 4600 ppm + He balance.

temperature (873 K). The presence of iron induces a slight increase of the NO conversion. On the other hand, the NO reduction is characterized by a different catalytic behaviour depending on the hydrocarbon, propane or propene, used as reductant. In the case of propane, the iron-containing catalysts are from three to six times more active than pure zinc manganite, i.e. ZnMn–Fe(0) catalyst, and, at least at lower temperatures, the activity increases on increasing the iron loading. These findings, as a whole, suggest that when propane is used as reductant not only the Mn³⁺ ions but also the Fe³⁺ ions act in the spinel as active sites. The slope of the activity levels, i.e. the apparent activation energy, E_a , is almost the same for the ZnMn–Fe(0), ZnMn–Fe(0.01) and ZnMn–Fe(0.05) catalysts (E_a ca. 102 ± 5 kJ mol^{−1}) while for the most rich in iron catalysts, i.e. ZnMn–Fe(0.10), E_a decreases to ca. 61 ± 5 kJ mol^{−1}. This remarkable decrease of the apparent activation energy suggests that the Fe³⁺ ions, at least in the most

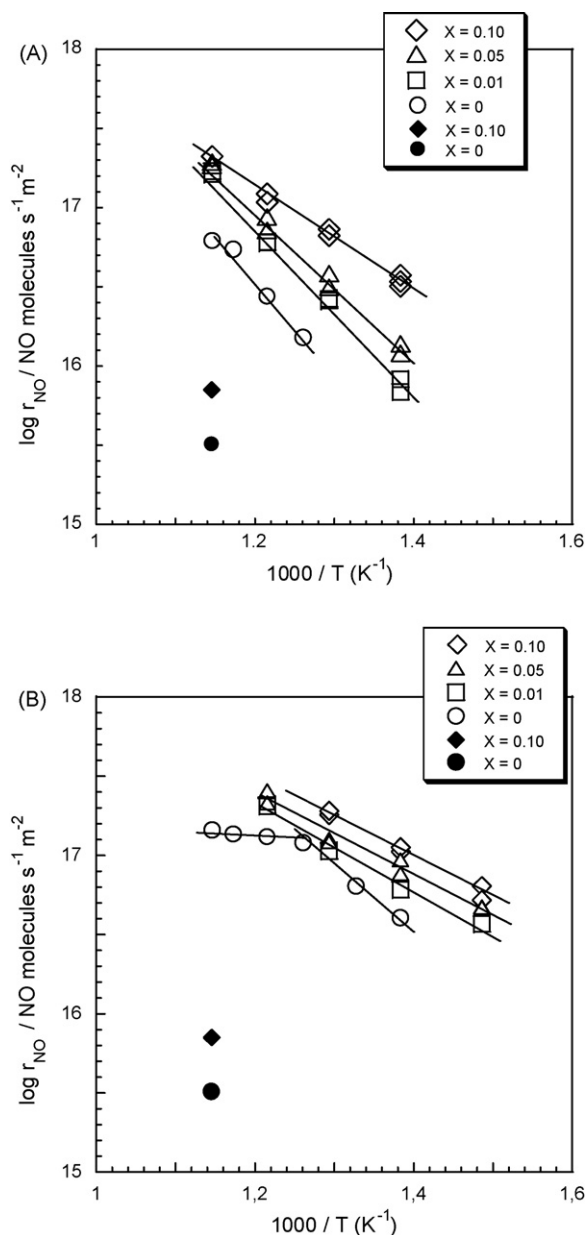
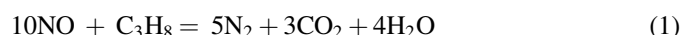


Fig. 2. Arrhenius plots of the NO reduction rates (open symbols) by C_3H_8 (A) and C_3H_6 (B) and activity levels for NO decomposition (closed symbols) over the ZnMn–Fe(x) catalysts. Reactant stream for the reduction: $[NO] = [C_3H_8] = [C_3H_6] = 4600$ ppm + He balance. Reactant stream for the decomposition: $[NO] = 4600$ ppm + He balance. In all cases GHSV = $60,000$ h^{-1} .

concentrated catalyst, are directly involved in the reaction mechanism. On the other hand, in the case of propene (see Fig. 2B) the presence of iron in the catalyst still improves the catalytic activity, but to a less extent if compared to the reaction with propane. The activity levels of the iron-containing catalysts are parallel to each other with a slope corresponding to an apparent activation energy, E_a , of 52 ± 5 $kJ\ mol^{-1}$. They are represented by straight lines in the overall range of temperature explored. By contrast, the activity level of the ZnMn–Fe(0) catalyst looks like a broken line having a point of discontinuity at about 773 K. This suggests that two temperature regimes occur in the case of reduction of NO by propene over the undoped catalyst, i.e. the ZnMn–Fe(0) [16,17]. They are characterized by

a different apparent activation energy: below 773 K E_a is about 75 ± 5 $kJ\ mol^{-1}$, a value larger than that found for the iron-containing catalysts, while E_a remarkably decreases for temperatures higher than 773 K.

In Fig. 3A and B the oxidation rate of propane, $r_{C_3H_8}$, and propene, $r_{C_3H_6}$, are compared with the reduction rate of NO, r_{NO} , over the ZnMn–Fe(0) and ZnMn–Fe(0.10) as representative catalysts. In the case of propane (see Fig. 3A), for all samples the rate at which NO disappears is about ten times higher than that of the hydrocarbon consumption. Moreover, regardless the catalyst composition, the selectivity to CO_2 is 1 in the whole range of temperature. Also the selectivity to N_2 is high and close to 1 at temperatures higher than 773 K. All these findings suggest that at the highest temperatures, when propane is the reductant, the stoichiometry of the main reaction is the following:



On the other hand, on decreasing the reaction temperature from 873 to 723 K, the $r_{NO}/r_{C_3H_8}$ ratio still remains close to 10 for the pure zinc manganite, ZnMn–Fe(0), but for the iron-containing catalysts it increases from *ca.* 10 to 20, indicating

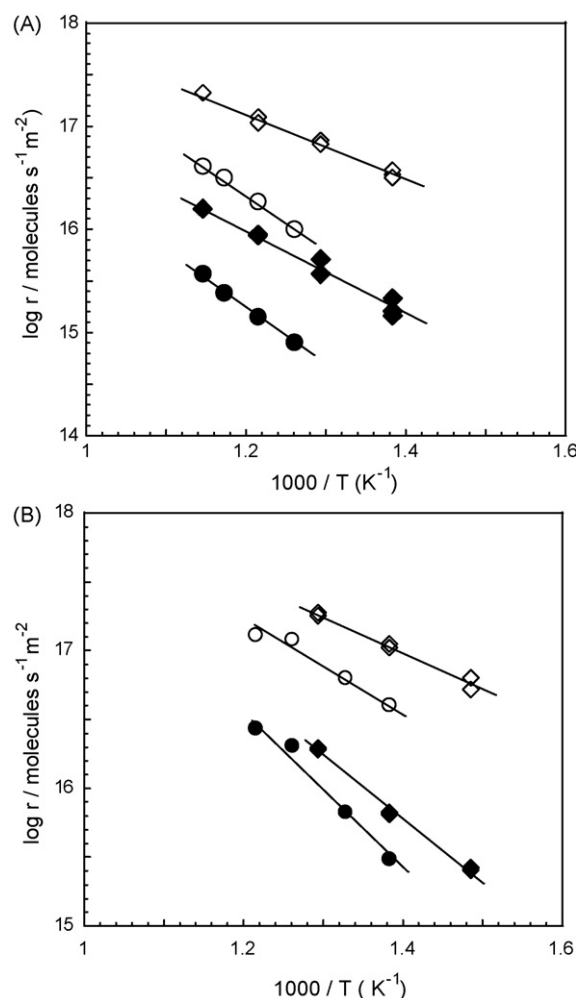


Fig. 3. C_3H_8 (A) and C_3H_6 (B) Arrhenius plots oxidation rates (closed symbols) compared to the corresponding NO reduction rates (open symbols) for the ZnMn–Fe(0) (\circ) and ZnMn–Fe(0.10) (\diamond) catalysts. Reactant stream: $[NO] = [C_3H_8] = [C_3H_6] = 4600$ ppm + He balance; GHSV = $60,000$ h^{-1} .

that, along with reaction (1), also the following reaction occurs:



When propene is the reductant, the selectivity to N_2 has a trend similar to that observed in the case of propane. At temperatures higher than 773 K the $r_{\text{NO}}/r_{\text{C}_3\text{H}_6}$ ratio is close to 9 suggesting that at these temperatures the main reaction is the following:



This is in agreement with selectivity to N_2 close to 1 found in the range of temperature 773–873 K.

However, for both undoped and Fe-doped zinc manganites, at temperatures lower than 773 K the $r_{\text{NO}}/r_{\text{C}_3\text{H}_6}$ ratio increases from *ca.* 9 to 18 indicating that, at lower temperatures, along with reaction (3) there is a relevant contribution of the following reaction:



The catalytic activity for the N_2O reduction by either propane and propene over the iron–zinc manganite catalysts is stable in terms of both N_2O conversion and selectivity to CO_2 during experiments prolonged for several hours. A representative example of the catalytic stability is reported in Fig. 4A and B showing plots of the N_2O conversion and CO_2 selectivity versus time on stream for the most rich in iron catalyst, i.e. $\text{ZnMn-Fe}(0.10)$, when propane (A) and propene (B) are used as reducing agents. Similar results were obtained for the undoped $\text{ZnMn-Fe}(0)$ catalyst. In Fig. 5A and B the Arrhenius plots showing the areal rate of the N_2O reduction by propane and propene and of the N_2O decomposition are reported for the $\text{ZnMn-Fe}(0)$ and the $\text{ZnMn-Fe}(0.10)$ catalysts, respectively. For comparison, in these figures the points corresponding to the rate of NO conversion for the NO decomposition have been also included. It appears that the N_2O decomposition occurs over all catalysts in the whole range of temperature explored (523–873 K) and its activity levels are much higher than that of the NO decomposition for which a measurable activity comes out only at the highest temperature (873 K). In the case of the undoped catalyst, the activity levels of the N_2O reduction and decomposition are close to each other and characterized by almost the same slope (see Fig. 5A). In particular, the activity levels corresponding to the N_2O decomposition and its reduction by propane are virtually coincident and slightly lower than the activity level of the N_2O reduction by propene. The presence of iron in the catalyst makes some changes to the above picture. This is well documented by the most rich in iron $\text{ZnMn-Fe}(0.10)$ catalyst (see Fig. 5B) taken as representative iron-containing catalyst. The Arrhenius plots corresponding to the N_2O reduction by propane and propene are characterized by parallel lines very close to each other and only slightly higher than that of the activity level of the N_2O decomposition. The slope of the activity level, i.e. the apparent activation energy, is different for the two reactions: it increases from E_a *ca.* $69 \pm 5 \text{ kJ mol}^{-1}$ for the N_2O decomposition to $E_a \approx 88 \pm 5 \text{ kJ mol}^{-1}$ for the N_2O reduction by the two hydrocarbons. The reactants disappearing rate ratios, $r_{\text{N}_2\text{O}}/r_{\text{C}_3\text{H}_8}$ and $r_{\text{N}_2\text{O}}/r_{\text{C}_3\text{H}_6}$, are almost equal to 10 and 9 for the N_2O reduction by propane and propene, respectively. Accordingly, the following stoichiometry:

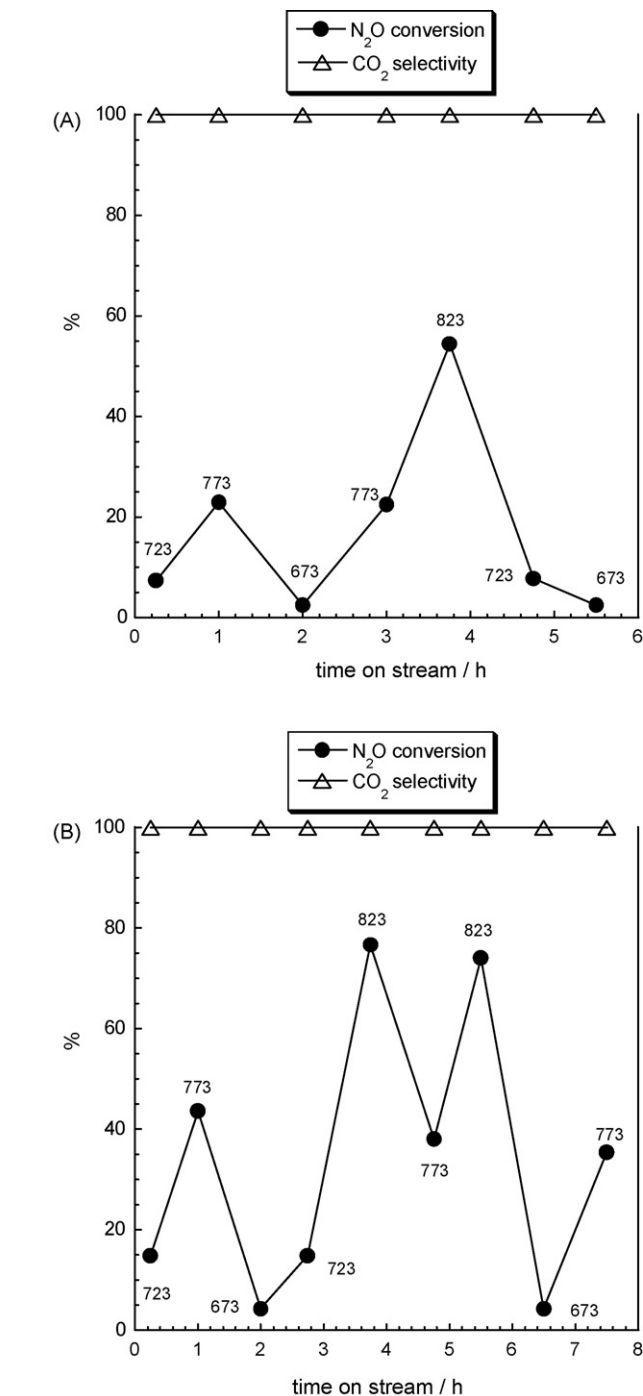
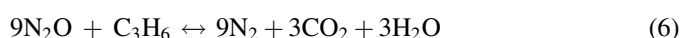


Fig. 4. Activity and selectivity to CO_2 vs. time on stream for the N_2O reduction by (A) propane and (B) propene: N_2O conversion at the temperatures (K) indicated as numbers inside the plots. Sample: $\text{ZnMn-Fe}(0.10)$; *ca.* 0.05 g. Reactant stream: $[\text{NO}] = [\text{C}_3\text{H}_8] = [\text{C}_3\text{H}_6] = 4600 \text{ ppm} + \text{He balance}$.

$r_{\text{N}_2\text{O}}/r_{\text{C}_3\text{H}_8}$ and $r_{\text{N}_2\text{O}}/r_{\text{C}_3\text{H}_6}$, are almost equal to 10 and 9 for the N_2O reduction by propane and propene, respectively. Accordingly, the following stoichiometry:



can be drawn for the reactions with the two hydrocarbons.

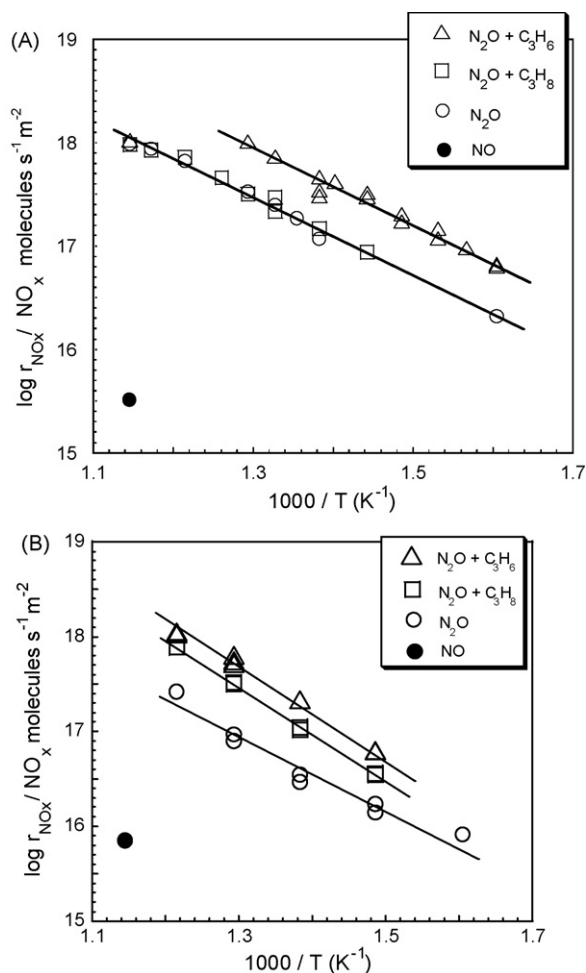


Fig. 5. Arrhenius plots of the N_2O decomposition and its reduction by C_3H_8 and C_3H_6 for (A) ZnMn-Fe(0) and (B) ZnMn-Fe(0.10) catalysts. For the sake of comparison the NO decomposition activity levels have been also reported. Reactant stream for the reduction: $[\text{N}_2\text{O}] = [\text{C}_3\text{H}_8] = [\text{C}_3\text{H}_6] = 4600 \text{ ppm} + \text{He}$ balance. Reactant stream for the decomposition: $[\text{N}_2\text{O}] = 4600 \text{ ppm} + \text{He}$ balance. In all cases GHSV = $60,000 \text{ h}^{-1}$.

4. Discussion

The catalytic data reported in this work clearly show, as a whole, that the iron-containing zinc manganites are effective catalysts for the reduction of either NO and N_2O by propane or propene and that there is an effect of the iron loading. In fact for both reactions the catalytic activity increases on increasing the iron content of the catalyst, in particular when propane is used as reductant. Also the decomposition of NO and N_2O proceeds over all catalysts and, as expected, the former reaction is much more difficult being a measurable catalytic activity found only at the highest temperature. Interestingly, if the decomposition of NO occurs much less efficiently than its reduction by hydrocarbons, by contrast the catalytic activity of the N_2O decomposition and its reduction by hydrocarbons are fairly equivalent. Indeed the study of the N_2O reactions not only reveals how much efficient are the iron–zinc manganites towards the N_2O abatement but it also helps to get more insight on the mechanism of the homologous NO reactions. The catalytic activity shown at 873 K by the ZnMn-Fe(0) catalyst in

the investigated reactions is a proof that Mn^{3+} ions are active sites for the NO , or N_2O , reduction by hydrocarbons and the N_2O decomposition as well. The role of Mn^{3+} ions as active species in NO involving reactions has been reported in literature. For instance, the Mn^{3+} ions located in the octahedral sites of the spinel structure may act as acid Lewis sites and are able to adsorb NO with a consequent formation of nitrosylic species [11]. The formation of dinitrosyl and mononitrosyl species upon contacting NO with Mn_2O_3 were reported by Yamashita and Vannice [9]. Isolated Mn^{3+} ions in octahedral symmetry are indeed considered responsible of the activity and high selectivity to N_2 in the selective catalytic reduction (SCR) of NO by NH_3 on low-loaded $\text{MnO}_x/\text{Al}_2\text{O}_3$ catalysts [20]. Our studies on the transition metal ion-doped zinc manganite systems shows that the catalytic behaviour is affected by the presence of Co [16], Cu [17] and Fe ions [this work], the effects depending on the nature of the hydrocarbon, on the nature of the transition metal ion as well as on its loading. In the case of NO reduction, propene appears to be more reactive than propane, this smoothing the effect of the iron loading on the catalytic activity (see Fig. 2). Moreover, the apparent activation energy, regardless the hydrocarbon used, decreases from the undoped to the iron-containing catalysts but it is much less sensitive to the iron content with propene than with propane. The effect of the iron loading on the catalytic activity is shown in Fig. 6 which reports, for propane and propene, the rates of NO conversion at 823 K (normalized with respect to the catalyst surface area) as function of the Fe molar ratio, χ_{Fe} ($\chi_{\text{Fe}} = \text{Fe}/(\text{Fe} + \text{Zn})$). The linear increase of the activity on increasing the iron loading suggests the following two important points: (i) the iron species at the catalyst surface (or a constant fraction of them) play an active role and (ii) their action add to that of Mn^{3+} ions. In the case of NO reduction by propane, the decrease of the apparent activation energy, E_a , from ca. 100 kJ mol^{-1} for the undoped catalyst, to 60 kJ mol^{-1} for the Fe -doped catalysts, is a further

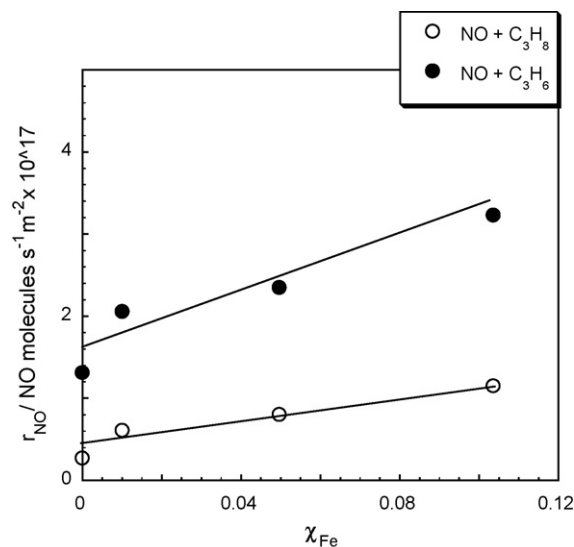
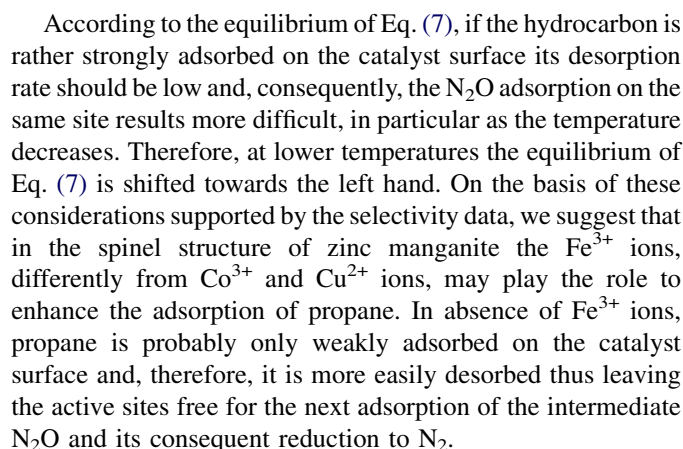


Fig. 6. NO reduction rates as function of the iron loading (χ_{Fe}), for the ZnMn-Fe(x) catalysts at 823 K when the reductant is propane (open symbols) or propene (closed symbols). Reactant mixture: $[\text{NO}] = [\text{C}_3\text{H}_8] = [\text{C}_3\text{H}_6] = 4600 \text{ ppm} + \text{He}$ balance.

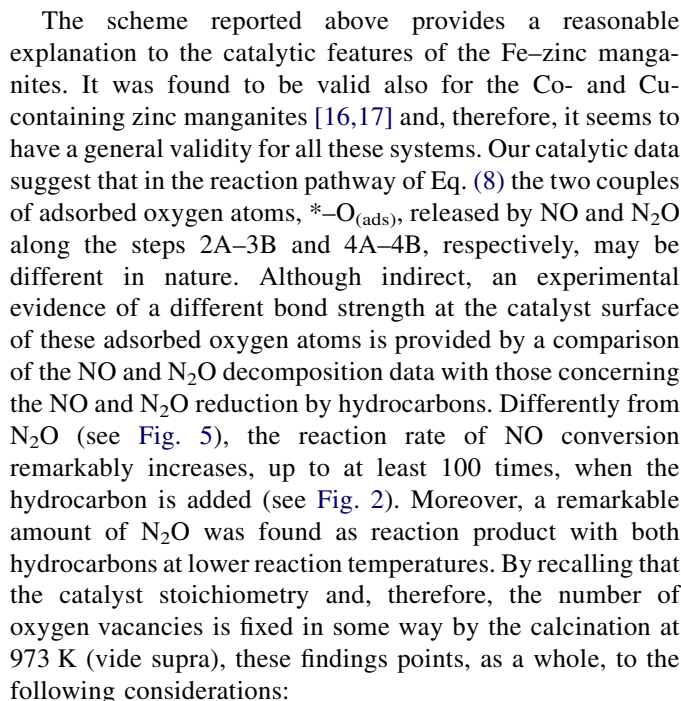
At first sight this result might appear surprising because an oxidized intermediate like N_2O is formed in presence of a reductant like propane, and even in presence of propene that is a stronger reductant than propane. The low selectivity to N_2 at lower reaction temperatures may be explained on the basis of a competitive adsorption between the reaction intermediate N_2O and the hydrocarbon (propane or propene):



Eq. (7)) is certainly enhanced. Moreover, with respect to propane, i.e. the homologous alkane, propene has the lowest C–H bond energies. This fact, together with the more strong adsorption on the catalyst surface, can give rise to the observed higher reactivity of propene in reducing NO if compared to propane.

The appearing of N_2O as intermediate in the reduction of NO by hydrocarbons is a clear evidence that in the first step of these reactions NO is adsorbed in some form on the catalyst surface and then desorbs as N_2O leaving an oxygen atom behind (vide infra). Then the adsorbed N_2O can desorb or react further, in this last case forming N_2 and leaving behind a second oxygen atom on the catalyst surface. N_2O can be also an intermediate of the NO decomposition [7].

Therefore we propose the following general reaction scheme:



- (i) During the NO reduction by propane, or propene, the formation of anionic vacancies and the consequent pairing of NO adsorbed molecules are not crucial for the reaction to occur, being the intermediate N_2O product already formed even at low temperature.

(ii) The permanence of N_2O in the gas phase when coming from NO is in contrast with the rapid decomposition when N_2O is alone, suggesting that the active sites, on which N_2O should adsorb to further decompose, are blocked to some extent not only by the hydrocarbon but very likely also by the surface oxygen atoms previously released by NO (step 2A or 3B).

In fact if these surface oxygen atoms would be as mobile as the oxygen released by N_2O (step 4A or 4B), or they were easily removed by the hydrocarbon, no intermediate N_2O should be observed in the gas phase. Indeed the absence of a significant increase of the activity level switching from N_2O decomposition to N_2O reduction by hydrocarbons (see Fig. 5) is a piece of evidence that the oxygen released in the step 4A, or 4B, should be a mobile surface species because its removal is almost insensitive to the presence of a reductant. Since steps 4A and 4B occur easily in presence or in absence of hydrocarbons, they should be ‘facile’ and, consequently, the N_2O decays cannot be the rate-determining step. Our results are in agreement with those reported by Yamashita and Vannice in very careful and detailed studies of the NO and N_2O decomposition over manganese oxides [6,7]. They found that Mn_2O_3 is the most active among the manganese oxides, thus confirming that the Mn^{3+} ions are the manganese ions effective for these reactions. Moreover, they reported that reaction mechanism of NO decomposition may involve the formation of N_2O followed by its rapid decomposition [7].

On the other hand, we are aware that also oxygen vacancies can play a role as active sites, as pointed out in the former pioneering study by Winter [21], and that, unlike N_2O , the pairing of NO molecules can represent an important step in the reaction mechanism of the NO decomposition. However, the results reported in the more recent papers by Yamashita and Vannice [6,7] specifically over manganese oxides, which have strong affinities with our catalysts, as well as our data suggest that the formation of anionic vacancies, or the NO molecules pairing, are not crucial steps in the reaction mechanism of the NO and N_2O reactions over the undoped and transition metal ion-doped zinc manganite catalysts.

Another intriguing result is concerning the stability of the Fe-doped catalysts under the reaction conditions that was checked by making an XRD analysis of the catalyst at the end of the catalytic runs. The XRD patterns of some representative catalysts recovered at the end of NO + C_3H_6 and N_2O + C_3H_6 catalytic runs are reported in Fig. 7A and B, respectively, together with XRD reference patterns of ZnMn_2O_4 , ZnO and MnO (see footnote 1). The XRD patterns of all catalysts after catalysis with propane well matched those of the as prepared materials indicating that the original structure is preserved and is stable under these conditions up to 873 K. This was in some way expected because similar findings were found also for the Co- and Cu-containing zinc manganites [16,17]. On the contrary, the Fe-containing zinc manganites preserved in propane the spinel structure even at the highest reaction temperature (873 K) differently from both the undoped and the Co-, Cu-doped zinc manganites that under the same experi-

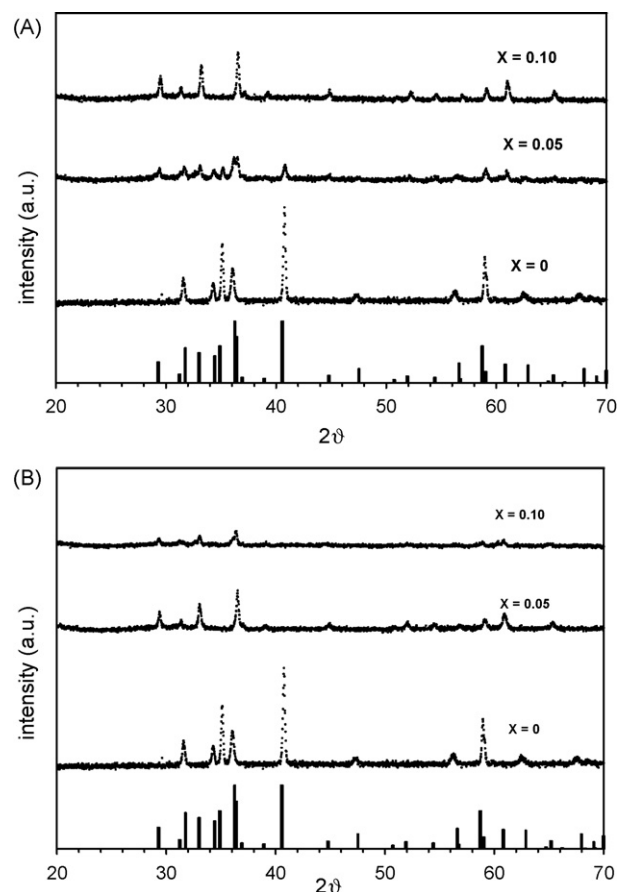


Fig. 7. XRD patterns for the $\text{ZnMn-Fe}(x)$ catalysts discharged after (A) the NO + C_3H_6 and (B) N_2O + C_3H_6 (B) catalytic runs at $T = 873$ K. For the sake of comparison the XRD reference patterns of ZnMn_2O_4 (empty bar), ZnO (solid bar) and MnO (dotted bar) are also reported (see footnote 1).

mental conditions lost the original spinel phase turning into a complex mixture of ZnO–MnO oxides as the reaction temperature increased over 773 K [16,17]. The catalyst stability of the Fe-containing catalysis seems to be depending on the iron content. In fact the $\text{ZnMn-Fe}(0.05)$ catalyst shows a partial reduction (see Fig. 7A). The higher resistance of the Fe-doped zinc manganites toward reduction in the catalytic runs where propene is used as reductant is perfectly paralleling the results of the reduction behaviour in H_2 . As evidenced by a TPR study [19], the Fe-doped zinc manganites were indeed less reducible in H_2 than the undoped or the Co-, Cu-doped catalysts. Therefore, the catalytic and TPR data agree and confirm that the spinel becomes more resistant toward reduction when Fe^{3+} ions are present in the structure. This property can be related to the chemistry of iron ions which, on the basis of the standard reduction potentials, result much more difficult to be reduced to metal with respect to cobalt and copper ions [22].

Finally, the partially disaggregated $\text{ZnMn-Fe}(0.05)$ and the totally disaggregated $\text{ZnMn-Fe}(0)$ catalysts are still characterized by a good catalytic activity (see Fig. 2B). This result was found also for the ZnMn-Co and ZnMn-Cu systems and it was at first surprising. The XRD analysis showed that, upon reduction, the original spinel phase turned into a mixture of MnO and ZnO oxides which can also form reciprocal $\text{Zn}^{2+}\text{-MnO}$ and

Mn²⁺–ZnO solid solutions [16]. It has been reported by Yao and Shelef [23] that the interaction of NO with the surface of MnO leads to the oxidation, even at room temperature, of Mn²⁺ to Mn³⁺ with the simultaneous chemisorption of NO on the resulting Mn₂O₃ surface. According to this valuable study, since Mn³⁺ ions are the active species in NO involving reactions, we suggested [16,17] that a similar oxidation can occur for the disaggregated catalysts in contact with gaseous NO during the reaction with propene. The regeneration of the Mn³⁺ active centre on the catalyst surface *via* oxidation by NO of the Mn²⁺ ions in the MnO–ZnO mixture, or in the Zn²⁺–MnO or Mn²⁺–ZnO solid solutions, could allow a sustained reduction of NO by the hydrocarbon.

5. Conclusions

Fe-doped zinc manganites are active catalysts for the reduction of NO, or N₂O, to N₂ by propane and propene. The catalytic data clearly indicate that Mn³⁺ ions, located in the octahedral sites of the spinel lattice, are the active species and the presence of Fe³⁺ ions enhances the catalytic activity for the NO reduction by C₃H₈ and C₃H₆. For these reactions iron plays an important role in the reaction mechanism by decreasing the apparent activation energy, in particular when propane is used as reducing agent. At 873 K the selectivity to N₂ and CO₂ is 1 and unaffected by the presence of iron. However, at lower temperatures, the selectivity to N₂ remarkably decreases over the iron-containing catalysts, N₂O being also formed. The reduction of N₂O by either propane and propene occurs efficiently over both undoped and Fe-doped catalysts with selectivity to CO₂ equal to 1 in the whole range of temperature explored. Compared to NO, the N₂O reduction by hydrocarbons is less affected by the doping of the catalyst. Moreover, the N₂O decomposition is characterized by a catalytic activity very similar to that of its reduction by C₃H₈, or C₃H₆, suggesting that the oxygen atom released by N₂O at the catalyst surface is easily removed even in absence of a reductant. On the contrary, the catalytic activity of the NO decomposition, for which iron has still a beneficial effect, results to be significantly lower than that of its reduction by hydrocarbons. The study of the NO and N₂O reactions, as a whole, suggest that in the NO reduction by hydrocarbons two different types of adsorbed oxygen may be involved in the reaction mechanism. One oxygen is more firmly retained at the catalyst surface and its removal is helped by the presence of the hydrocarbon, the other one is characterized by a high mobility and therefore it is insensitive to a reductant. All catalysts are stable up to 873 K when propane is contained in the reaction stream. When propene is the reductant, the undoped catalyst collapses above 773 K forming a complex

mixture of ZnO and MnO oxides while the presence of iron increases the catalyst stability preventing the spinel reduction even at the highest reaction temperature.

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